

# Polymer microstructure optimization aided by STXM spectromicroscopy

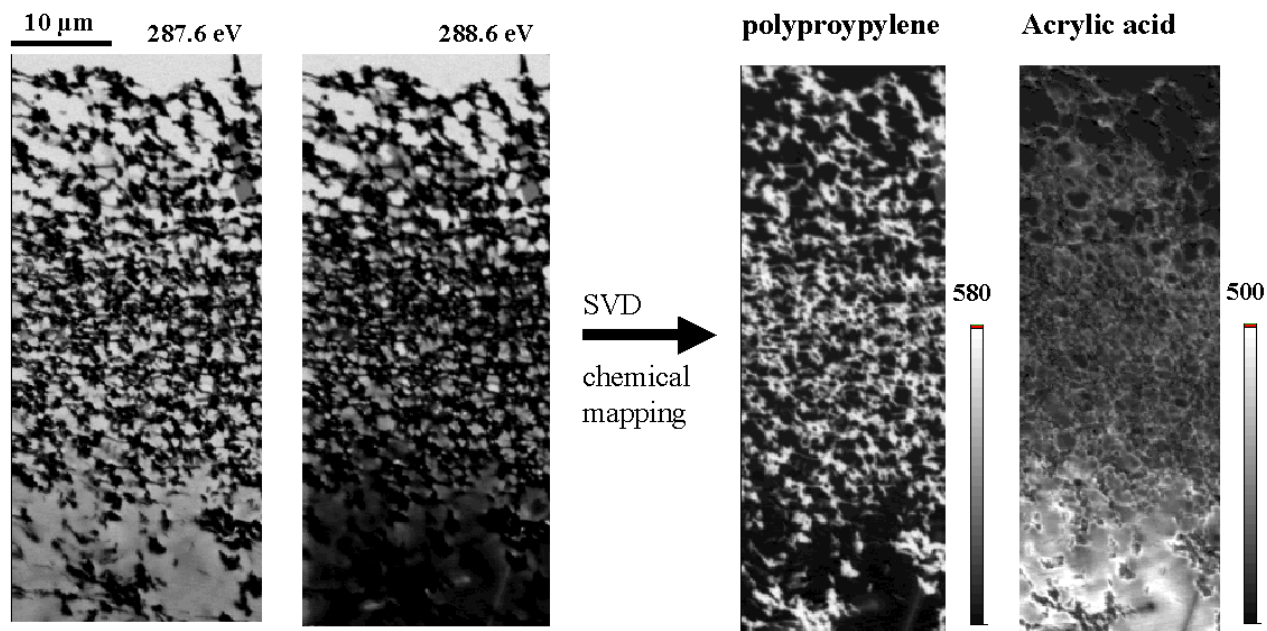
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## INTRODUCTION

Quantitative, spatially resolved chemical analysis which is sensitive to molecular structure (e.g functional group composition) is needed to help understand and optimize many modern polymer systems. Correlating quantitative chemical microanalysis with physical, chemical and mechanical properties is needed for materials optimization. Scanning transmission X-ray microscopy (STXM) is a powerful tool for sub micron chemical analysis of polymers [1,2]. NEXAFS spectroscopy at high spatial resolution and energy selective imaging provide sensitivity to many sample properties such as local chemical composition, orientation, interface chemistry, etc. The STXM technique can be adapted to many different sample environments including fully hydrated or solvated materials. The intrinsic power of STXM spectromicroscopy is further enhanced by acquisition strategies such as linescans or image sequences, as well as sophisticated analysis methodologies which simultaneously exploit the spatial and spectral domains to achieve composition mapping [3]. We are using the beamline 7.0.1 STXM to study a wide range of polymer problems as part of a strategic program to explore and demonstrate its benefits in aiding polymer microstructure optimization.



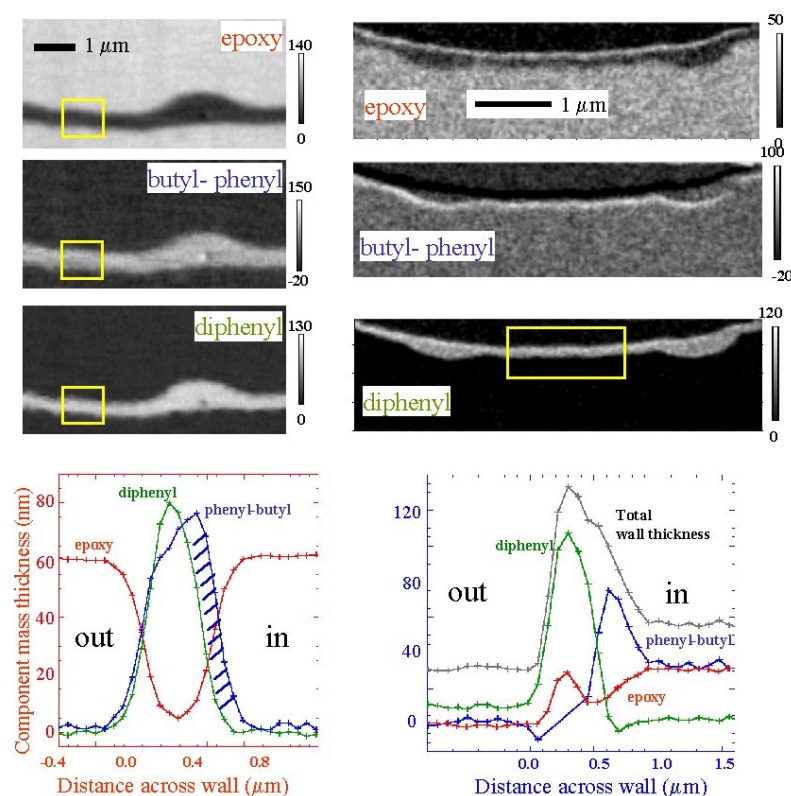
**Fig. 1** Transmission images at 287.6 eV (only PP absorbs) and 288.6 eV (both PP and AA absorb) of a water filtration membrane consisting of polyacrylic acid (AA) embedded in polypropylene (PP). The wet sample was frozen and cryo-microtomed to 500 nm sections which were examined at room temperature in the fully hydrated state, enclosed between two silicon nitride windows. The images at 11 energies were aligned, converted to OD scales and processed using singular value decomposition (SVD) to produce quantitative spatial distributions of the PP and AA (component maps). The z-scales of the component maps are in units of nm\*(density). [10]

## RESULTS AND DISCUSSION

Many different systems are under study, in part to identify the range of problems that are suited for STXM study. Two examples are presented in somewhat more detail in the sections below. Other studies have been carried out in the past year on: polyurethane phase segregation (with Ade, Dow group) [4], pattern formation in confined free standing PS-PI-PS trilayer films (with Ade, Dutcher) [2,5], core-shell microspheres [6,7], polystyrene-polymethylmethacrylate blends [8,9] and copier toner particles (with Ricoh).

**Analysis under water: Water filtration membranes.** One of the largest advantages of X-ray microscopy relative to electron microscopy is the ability of the photon in - photon-out STXM technique to examine material in a water environment - fully hydrated polymeric membranes, cells, clay minerals, food, milk etc. An example of this is given in **Fig. 1** which shows results from a study of the distribution of a polyacrylic acid electrolyte gel embedded in a polypropylene support membrane [10]. Mapping the acrylic acid distribution relative to the polypropylene support allows better understanding of the links between loading methodologies and the membrane performance in filtering industrial wastewater. Attempts to map this distribution using environmental SEM or AFM were not successful. Confocal microscopy is also being used in this project; the higher spatial resolution and chemical specificity of the STXM nicely complements the capability of confocal microscopy of stained samples to perform chemically sensitive 3-dimensional imaging.

**Controlling microstructure: polyurea capsule walls.** Polymers are frequently used to encapsulate other chemicals for a variety of purposes - packaging, transport, controlled release of drugs, nutrients, pesticides, pheromones etc. We have used STXM to detect and quantify the chemical structure of sub-micron wide walls of polyurea capsules [2,11]. The capsules are produced by interfacial polymerization - reaction between amine and isocyanate at the interface between organic and aqueous phases in a dispersion of a 1:10 mixture of MDI-isocyanate and xylene in an aqueous solution of ethylene diamine. In addition to the amine-isocyanate reaction which produces an asymmetric aromatic-aliphatic urea, there is a competing reaction between the MDI-isocyanate and water which produces a symmetric di-aromatic urea. The temporal and spatial aspects of this competition can lead to formation of gradients in the chemical structure of the walls of these capsules. These are postulated to occur due to (i) pre-reaction with water in an amine-free emulsification step which results in an outer skin of symmetric urea, (ii) preferential diffusion and reaction of amine relative to water during the reaction, which leads to a central region rich in asymmetric urea; and (iii) post-synthesis curing when capsules are stored in water, in which water enters the capsule and reacts with residual isocyanate to form inner wall structures rich in symmetric urea. **Fig. 2** shows chemical compositional maps and profiles of the structure of the capsule walls from two different polyurea capsule formulations. In one, a very short emulsification period was used and the outer skin of symmetric urea is relatively thin. In the other emulsification was carried out for an extended 2 hour period. Here the outer skin contains only symmetric urea, with the asymmetric urea being found only in the inner half of the capsule wall. The distributions of asymmetric (amine reaction) and symmetric (water reaction) ureas across these two membranes derived from C 1s STXM image sequences are qualitatively consistent with the model of competitive reactions although the STXM does show that the water based reaction continues throughout the process, and the amine reaction fills in porosity in the initially formed symmetric skin, so that both symmetric and asymmetric components occur throughout most of the capsule wall. Analysis of diffusion and reaction kinetics is now in



**Fig. 2** C 1s STXM study of 2 different polyurea capsules [11]. The upper part displays derived component maps of the 3 chemical components: the epoxy support; asymmetric urea, modeled as butyl-phenyl urea; and symmetric polyurea, modeled as diphenyl urea. The lower part plots component mass thickness profiles integrated orthogonal to the capsule wall in the indicated region. The right sample was prepared with a longer emulsification step, which leads to a thick outer skin of symmetric urea (note differences in spatial scales. (ALS BL 7.0 STXM)

progress to model quantitatively the capsule wall formation process. The ability to fabricate structured walls with controlled chemical gradients could allow significant improvements in capsule properties for specific applications.

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